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First Quarterly Report

on

STUDY OF USE OF AUXILIARY ELECTRODES IN SILVER CELLS

1 February, 1964 - 1 May, 1964

Contract No. NAS5 - 3669

Prepared by

General Electric Company

Advanced Technology Laboratories  
Schenectady, New York

for

Goddard Space Flight Center  
Greenbelt, Maryland

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## SUMMARY

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The primary objective of this program is to investigate the use of auxiliary electrodes in primary and secondary silver-zinc cells and to modify commercially available silver-zinc cells for testing by NASA-Goddard. Additional work areas include the continuation and the completion of testing of silver-cadmium cells with auxiliary electrodes remaining from Contract NAS-5-2817, and the investigation of electrochemical techniques for recombining hydrogen evolved from primary silver-zinc cells used in satellite power supply systems.

Project work was started during the second week of March. The initial work consisted largely of establishing experimental work plans and fabricating test cells to determine hydrogen and oxygen recombination rates for various auxiliary electrode material compositions and geometry.

The silver-cadmium cells from the previous contract were returned to cyclic testing but this was discontinued when it was observed that the capacity of the cells had decreased to less than twenty-five percent of their original value. New cells will be fabricated and put on cycling tests to accumulate additional data.

AUTHOR:

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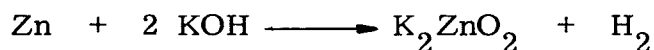
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## 1.0 INTRODUCTION

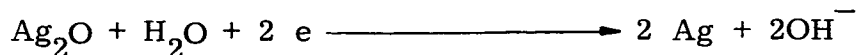
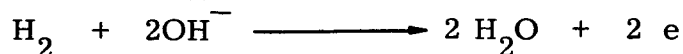
This report covers the work done during the first quarter of a twelve-month program to investigate the use of auxiliary electrodes in silver-zinc cells. Two additional work areas are the continuation and completion of cyclic tests of silver-cadmium cells with auxiliary electrodes from a previous contract (NAS5-2817) and the investigation of the feasibility of recombining hydrogen evolved from a silver-zinc satellite power supply system by means of an electrochemical cell.

Of primary concern, in the application of auxiliary electrode control to silver-zinc cells, is poisoning the zinc electrode with platinum from the auxiliary electrode which catalyzes the self-discharge reaction of the zinc electrode:



It is believed that the danger of platinum migration to the zinc electrode is small since, (1) the binder of the electrode has been very effective in holding the catalyst in place and has shown no deterioration in electrodes used for 10-14 months; (2) the platinum is in a highly insoluble form and has shown no tendency to go into solution when the electrode is used at current densities below 50 ma/cm<sup>2</sup>; (3) the barriers used in silver cells for blocking silver migration are equally effective for platinum, since platinum compounds are more easily reduced or absorbed than silver.

Although the auxiliary electrode has been used primarily as an oxygen electrode in silver-cadmium applications, it should be noted that there is no basic reason for an auxiliary electrode being operated only as an oxygen electrode. It can also be operated as a hydrogen electrode. For use as a hydrogen electrode, the auxiliary electrode would be connected to the positive (silver oxide) electrode in use, the recombination reactions being:



With this type of auxiliary electrode operation, the cell should be designed to be negative plate limiting, so that hydrogen is preferentially evolved on charging. The use of a hydrogen recombination system is desirable for silver-zinc cells, since there is an evolution of hydrogen during the cell stand and discharge that leads to pressure build-up in many applications.

The use of two auxiliary electrodes -- one for oxygen recombination which is attached to the negative electrode, and one for the recombination of hydrogen which is attached to the positive electrode -- is possible.

The principal advantage of this dual system is that gassing of either hydrogen or oxygen would be taken care of. Also, the use of a platinum containing catalyst for the oxygen electrode is not needed thus removing the possibility of zinc electrode degradation by coupling through the external circuit. This non-platinum containing type of electrode was originally proposed for use in silver-cadmium cells, but was abandoned in favor of the currently used one which can recombine small amounts of hydrogen directly, since this property was useful and presented no problems in use in silver-cadmium cells.

Another potential problem area is the possible poisoning of the auxiliary electrodes by interactions with both silver and zincate ions present in the electrolyte phase of these cells. At present, there is no evidence that either will degrade the electrode for oxygen or hydrogen recombination. This aspect, however, will be investigated.

An outline of the program work content by tasks is given in Table I.

## 2.0 DISCUSSION

The work during the first quarter was largely concerned with establishing overall experimental plans for the program and fabrication of test cells for obtaining design data for auxiliary electrodes to be used in modifying the silver-zinc cells. Accomplishments and plans are discussed by Tasks in the following sections.

### 2.1 Silver-Cadmium Cells - Task I

Six 5.0 Amp-hour cells from the previous contract were returned to cyclic testing using a 12 hour cycle; discharge for 0.5 hours at 2.5 amp. and charge for 11.5 hours at 0.12 amp. The tests were discontinued after two weeks when it was observed that the capacity of the cells ranged from 5 to 25% of the original 5.0 amp-hour value.

New cells are being constructed and will be put on test to obtain additional design data. These cells are fabricated from Yardney YS-5 electrode packs consisting of four silver and five cadmium electrodes. The auxiliary electrode consists of a nickel wire mesh coated with a thin layer of electrode catalyst, electron carrier and binder.

The dimensions of the auxiliary electrode are the same as the dimensions of the YS-5 electrodes. The auxiliary electrode is placed against one of the cadmium electrodes with a Nylon separator (Pellon 2505W) between the two. The gas side of the auxiliary electrode is separated from the Lucite cell case by a piece of polyethylene grid. This material is Vexar Plastic Netting (Vexar Division, E. I. Dupont de Nemours, Buffalo, New York) diamond pattern 4/4-30-90-PE-3.

TABLE I  
Program Tasks

Task I - Silver-Cadmium Cells.

The 5.0 amp. hr. test cells from the previous contract (or new ones) with auxiliary electrodes will continue to be cycled at room temperature with periodic monitoring of cell capacity and continuous monitoring of cell pressure.

Task II - Silver-Zinc Cells.

Perform studies on the use of auxiliary electrodes for recombination of hydrogen and oxygen as a function of operating parameters to obtain design data to modify commercial silver-zinc cells of 3.0 amp. hr. capacity.

- A. Study the effect of auxiliary electrode materials on the self-discharge of the zinc electrode in both the electrically coupled and uncoupled condition.
- B. Study recombination of hydrogen during charge, stand, and discharge by an auxiliary electrode connected to the positive cell electrode.
- C. Study the recombination of oxygen during charge and stand on an auxiliary electrode when connected to the negative cell electrode.
- D. Study the effect of silver and zincate ions on the hydrogen and oxygen recombination by auxiliary electrodes.

Task III - Modification of Silver-Zinc Cells.

Incorporate auxiliary electrodes into fifty 3.0 amp. hr. commercially available silver-zinc cells.

Task IV - Hydrogen Recombination Cell.

Investigate the feasibility of electrochemical recombination of hydrogen evolved from silver-zinc satellite power supply systems. Cells employing AgO and CuO will be investigated initially.



## 2.2 Silver-Zinc Cells

This task is concerned with obtaining design data on the suitability of various auxiliary electrode compositions for hydrogen and oxygen recombination. Factors which will be evaluated are: the effect of auxiliary electrode materials on self-discharge of zinc electrode, rates of recombination of hydrogen and oxygen at various levels of gas pressure, and the effects of silver and zinc ions on the rate of recombination.

### 2.2.1 Self-discharge of Zinc Electrode

The composition of the conventional auxiliary electrodes for oxygen recombination was found to be unsatisfactory for this function in silver-zinc cells. The platinum contained in these electrodes promotes the rapid discharge of the zinc electrode when electrically connected through a low resistance load. In one test a zinc electrode from a 3.0 amp-hour Yardney silver-zinc cell (Model PM-3) was completely discharged in approximately 8 hours when connected to an auxiliary electrode through a one ohm load. The dimensions of the auxiliary electrode were the same as the dimensions of the electrodes in the PM-3 cell pack.

More precise measurements will be made to determine if the conventional electrodes cause a significant increase in hydrogen evolution when coupled to the silver electrode and in the uncoupled condition.

### 2.2.2 Hydrogen Recombination Studies

These studies will be made with test cells employing two working electrodes and a mercury-mercuric oxide reference electrode. Hydrogen will be generated at one of the working electrodes (cadmium or zinc) and recombined at the other which will be an auxiliary electrode type.

The cadmium electrode (SAFT-VO Type) will be used first to establish performance reference data in the absence of side reactions which may occur with the zinc electrodes. The zinc electrodes will be taken from Yardney PM-3 or HR-3, 3.0 amp. hr. cells. Area dimensions of the auxiliary electrode will be the same as the zinc electrodes.

Testing will be accomplished by first charging the cells to various pressure levels with hydrogen (700, 100, 10, 0 mm. Hg). The cells will then be sealed and charged at rates ranging from C/20 to C/5 at room temperature. Tests will start with the zinc or cadmium electrode fully charged and will be run for at least 8 hours at each charging rate. Cell pressure and electrode potentials will be continuously monitored and recorded. Pressure rises will indicate either inability of the auxiliary electrode to recombine hydrogen at the rate of production or if potentials increase the generation of oxygen at the auxiliary electrode. Gas samples will be analyzed for

composition to determine if the latter mechanism is contributing to observed pressure increases. Eight test cells, four with cadmium electrodes and four with zinc electrodes were fabricated.

### 2.2.3 Oxygen Recombination Studies

Test cells for these studies will be of the same design as those used for the hydrogen recombination rate studies. The auxiliary electrode composition will exclude platinum in view of the previous results which show that this material promotes the self-discharge of the zinc electrode when electrically coupled.

Electrodes consisting of silver powder and plain silver mesh will therefore be evaluated for this function. Oxygen generating electrodes will be either SAFT-VO Type nickel electrodes or silver oxide electrodes taken from Yardney PM-3 or HR-3 cells.

Test procedures and conditions will be the same as for the hydrogen recombination tests, except that initially cells will be charged with oxygen with pressures ranging from 700 to 0 mm Hg.

Fabrication of eight test cells for these experiments was started during the quarter.

### 2.2.4 Silver and Zincate Ion Effects

The effect of these two ions if any on the recombination rates for both oxygen and hydrogen will be determined by additions of these to the electrolyte at selected concentration levels. These tests will be done with test cells employing the cadmium or nickel electrodes first and then with zinc and silver oxide electrodes if necessary.

## 2.3 Hydrogen Recombination Cell

The objective of this task is to assess the feasibility of electrochemically recombining the hydrogen evolved from a silver-zinc satellite primary power supply system. The nominal recombination capacity is to be 200 cc. of  $H_2$  per hour.

This function is presently performed by adsorption of the hydrogen on palladium. A primary goal is to reduce the weight of the system. The adsorption capacity of palladium at ambient temperature and one atmosphere partial pressure of hydrogen is approximately 177 g Pd/g  $H_2$ .

Silver (II) oxide and copper (II) oxide appear to be attractive cathode materials from the standpoint of electrochemical reactivity and mass equivalent weight. The equivalent weight for AgO is 113 g/g  $H_2$  and for CuO, 40 g/g  $H_2$ .

Test cells consisting of the above cathode materials and a conventional auxiliary electrode as a hydrogen electrode will be constructed and tested over the temperature range of 10 to 40°C and current densities of 5 to 20 ma/cm. Hydrogen pressure for these first tests will be maintained at one atmosphere. The electrolyte concentration will be 31% potassium hydroxide.

Utilization of cathode material for varying electrode thickness will be evaluated as function of current density and temperature. The other important design consideration is to evaluate the effect of product water accumulating in the electrolyte phase for prolonged operating times. It may be possible to accumulate the major portion of product water in a separate container and avoid electrolyte dilution.

The data from the above studies will be used to build a minimum weight prototype cell to demonstrate the concept and capability of operation for one to two months.

### 3.0 PROGRAM FOR NEXT QUARTER

The major portion of the effort will be on the hydrogen and oxygen recombination studies under Task II. The silver-cadmium cells will be put on test during the latter part of the quarter. Fabrication of the hydrogen recombination test cells for Task IV will be started by the end of the next quarter.